diethoxybutane (2,3-dimer) was 2.57 units, that of the 1,3-dimer was ≤ 0.09 units, and the 1,4-dimer was not observed. Similarly, G(ethyl sec-butyl ether) = 0.74 and G(ethyl n-butyl ether) = 0.03. There is some doubt about the exact yields of the minor products, but the results indicate that the value of the ratio of the steady-state concentration of $CH_3\dot{C}HOC_2H_5$ to that of $\dot{C}H_2CH_2OC_2H_5$ was about 40 to 1. If this difference is

attributed to the difference in the activation energies of the two abstraction reactions

$$R + CH_3CH_2OC_2H_5 \longrightarrow RH + CH_3\dot{C}HOC_2H_5 \quad (24)$$
$$\longrightarrow RH + \dot{C}H_2CH_2OC_2H_5 \quad (25)$$

then $\Delta E = (E_{25} - E_{24}) = 2.4$ kcal./mole. This is in good agreement with the corresponding value $\Delta E = 2.7$ kcal./mole in the ethanol system.[7]

Radiolysis of Diethyl Ether. II. Deuterium-Substituted Ethers in the Gas and Liquid Phases[1]

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The G values of the major products of the γ-radiolysis of diethyl ether vapor at 25° and a dose of 3 × 10²⁰ e.v./g. are: hydrogen, 6.4; 2,3-diethoxybutane, 2.4; ethylene, 2.1; acetaldehyde, 1.4; methane, 1.3; ethyl isopropyl ether, 1.0; formaldehyde, 0.9; ethyl sec-butyl ether, 0.8; ethanol, 0.7; $G(-C_2H_5OC_2H_5) = 11.2$, based on the carbon in the measured products; G(excess H_2 in products) = 1.7. The yields of acetaldehyde and ethyl vinyl ether (G = 0.4 at 19 × 10²⁰ e.v./g.) decreased with increasing dose. The value of G(−ether) in the vapor phase is nearly the same as that in the liquid phase, although the product distribution is quite different in the two phases. Ether molecules, on the average, break into smaller fragments in the gas than in the liquid phase radiolysis. For the reactions $R + M \xrightarrow{k_a} RH + R'$ and $R + R \xrightarrow{k_c} R_2$, k_a/k_c is smaller in the vapor than in the liquid phase. Comparison of the product yields from the radiolysis of $(C_2H_5)_2O$, $(CD_3CH_2)_2O$, $(CH_3CD_2)_2O$, and $(C_2D_5)_2O$ showed that α-C–H bond cleavage was most important in hydrogen and methane formation, and β-C–H cleavage was most important in ethylene formation although both types of cleavage made significant contributions to the formation of all three products.

Introduction

The γ-radiolysis of liquid diethyl ether was reported earlier.[2] The present article describes a brief study of the γ-radiolysis of the ether in the gas phase and also reports the influence of phase on the hydrogen–deuterium content of some of the gaseous products from various deuterium-substituted diethyl ethers.

Baxendale and Gilbert[3] found the values $G(H_2) = 6.75 \pm 0.05$ and $G(CH_4) = 3.55 \pm 0.15$ for the γ-radiolysis of diethyl ether vapor. The yields of the other products were not measured. The conditions of the experiments were 116°, 140 and 470 mm. pressure,

dose rate = 3 × 10¹⁷ e.v./g. hr. (N₂O dosimetry), dose ≈ 10¹⁸ e.v./g.

Experimental

Most of the materials and procedures were described earlier.[2] Only new materials and techniques will be described here.

Three deuterated ethers were obtained from Merck Sharp and Dohme of Canada Ltd: $(C_2D_5)_2O$ (ether-d_{10}); $(CD_3CH_2)_2O$ (ether-β-d_6); $(CH_3CD_2)_2O$ (ether-α-d_4). The isotopic impurities of the ethers were measured by n.m.r. analysis and are listed in Table I.

Table I. Isotopic Impurities in the Deuterated Ethers

Ether	Impurity	Atom %[a]
$(CD_3CD_2)_2O$	α-H	9.0
	β-H	0.6
$(CD_3CH_2)_2O$	α-D	25
	β-H	18
$(CH_3CD_2)_2O$	α-H	4.2
	β-D	4.3

[a] For example, 100(α-H)/(α-H + α-D) is the atom % of H impurity in the α position.

The gas phase radiolysis cells were 500-ml. Pyrex bulbs with break-seals. Each cell contained about 0.7 g. (0.5 atm.) of sample. The irradiation temperature was 25 ± 3°, and the dose rate was 6 × 10¹⁹ e.v./g. hr. Unless otherwise stated, the liquid and the vapor samples received a dose of 3.5 × 10²⁰ e.v./g.

Liquid phase dosimetry was done with the Fricke dosimeter. Vapor phase dosimetry was done with ethylene, using $G(H_2) = 1.28$.[4] Sufficient ethylene was placed in the bulb that the electron density of ethylene was approximately the same as that of ether in the ether samples.

The products were analyzed by the same techniques as those reported in the previous paper,[2] except that the gaseous products were analyzed by mass spectrom-

(1) This work received financial assistance from the National Research Council of Canada.

(2) M. K. M. Ng and G. R. Freeman, *J. Am. Chem. Soc.*, **87**, 1635 (1965).

(3) J. H. Baxendale and G. P. Gilbert, *Discussions Faraday Soc.*, **36**, 186 (1963).

(4) R. A. Back, T. W. Woodward, and K. A. McLauchlan, *Can. J. Chem.*, **40**, 1380 (1962).
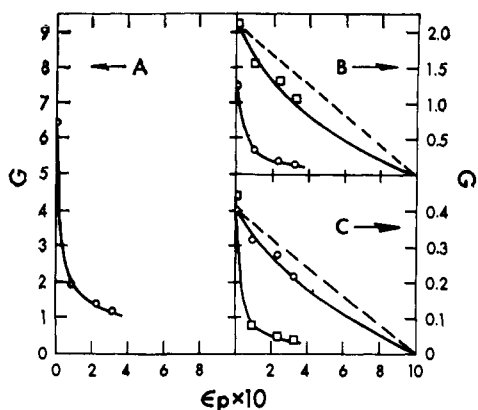
Figure 1. Gaseous product yields as a function of 1,3-pentadiene concentration (gas phase radiolysis). The dashed lines refer to $G_{expected}$. Dose $= 3.5 \times 10^{20}$ e.v./g.; $\epsilon_p =$ electron fraction of 1,3-pentadiene. A: H_2. B: O, CH_4; □, C_2H_4. C: O, CO; □, C_2H_6.

etry instead of by gas chromatography. For formaldehyde analysis of the vapor samples, the sample cell was cooled in ice water before it was opened. After breaking open the cell, 5 ml. of distilled water was introduced into it, the cell shaken, and the ether allowed to evaporate. The solution was analyzed by a chromotropic acid method.[5] Freezing the sample was avoided to prevent polymerization of the formaldehyde.

Results

Gas Phase Radiolysis of "Light" Diethyl Ether. Most of the product yields were measured at doses of 1.0, 2.0, and 3.5 × 10²⁰ e.v./g. and were independent of dose over this range. The G values listed in Table II

Table II. Gas and Liquid Phase Radiolysis Product Yields

Product	G^a Gas phase	G^a Liquid phase[2]
Hydrogen	6.4	3.4
2,3-Diethoxybutane	2.4	2.6
Ethylene	2.1	0.6
Acetaldehyde	1.4	0.2
Methane	1.3	0.4
Ethyl iso-propyl ether	1.0	0.07
Formaldehyde	0.9	0.0
Ethyl sec-butyl ether	0.83	0.74
Ethanol	0.65	2.1
Ethane	0.44	1.3
Carbon monoxide	0.40	0.07
Ethyl vinyl ether	0.4	1.1
Diethoxymethane	0.22	0.08
Propane	0.14	0.08
Ethyl methyl ether	0.14	0.0
Acetal	0.09	0.14
Acetylene	0.03	0.01
(−ether)[b]	11.2	11.3[c]

[a] All yields refer to the dose 3 × 10²⁰ e.v./g. except those of acetaldehyde (5 × 10²⁰ e.v./g.) and ethyl vinyl ether (19 × 10²⁰ e.v./g.). The yields of the latter two products decrease with increasing dose. [b] Based on the amount of carbon in the measured products. [c] All the liquid phase products are not listed in this table.

are the averages of three measurements. Because of analytical difficulties, acetaldehyde and ethyl vinyl

(5) J. M. Ramaradhya and G. R. Freeman, *Can. J. Chem.*, 39, 1836 (1961).

ether had to be measured at higher doses. The yield of acetaldehyde decreased from $G = 1.4$ at 5×10^{20} e.v./g. to 1.0 at 19×10^{20} e.v./g. The yield of ethyl vinyl ether was $G = 0.4$ at 19×10^{20} e.v./g.; *i.e.*, the final ethyl vinyl ether concentration was 0.09 electron %. However, when diethyl ether was radiolyzed in the presence of 0.3 % of ethyl vinyl ether, the latter was destroyed at a rate which corresponded to $G = 0.74$ at 5.0×10^{20} e.v./g. The steady-state concentration of ethyl vinyl ether in diethyl ether under these conditions of radiolysis was in the vicinity of 0.2 %. Thus, the value of G(ethyl vinyl ether) would be greater than 0.4 at doses below 19×10^{20} e.v./g.

The product yields from the liquid phase radiolysis of diethyl ether[2] are included in Table II for comparison. The product distribution is quite different in the two phases.

The effects of 1,3-pentadiene on the gaseous product yields are shown in Figure 1. The formation of ethylene and of carbon monoxide is slightly inhibited, whereas the formation of hydrogen, methane, and ethane is greatly inhibited.

The inhibition of the formation of three major liquid products is shown in Table III. The yields of all three products are greatly reduced by 1,3-pentadiene.

Table III. Inhibition of Liquid Product Formation in Gas Phase Radiolysis

Product	$\epsilon_p = 0$	G $\epsilon_p = 0.086$	$\epsilon_p = 0.23$	$\epsilon_p = 0.32$
2,3-Diethoxybutane	2.38	<0.2	<0.2	<0.2
Ethyl sec-butyl ether	0.83	0.14	<0.09	<0.09
Ethanol	0.65	0.2	0.2	<0.1

Deuterated Ethers. Each ether was irradiated in the gas and liquid phases in the presence and absence of an electron fraction of 1,3-pentadiene equal to 0.17. This concentration of pentadiene essentially completely suppresses the free-radical contributions to the product yields.

The yields and isotopic composition of the product hydrogen from the various samples are listed in Table IV. The total hydrogen yield is decreased more by deuteration of ether in the α-position than by deuteration in the β-position, in both the liquid and gas phases (Table IV). Furthermore, the percentage of D in the hydrogen produced from ether-α-d_4 was greater than in that from ether-β-d_6 (Table IV). The percentage of D in the product hydrogen decreased slightly from the liquid to the gas phase radiolysis, and the effect was more pronounced with ether-α-d_4 than with ether-β-d_6.

The yields and isotopic composition of the methanes from the different samples are given in Table V. The methane analyses from the gas phase samples of ether-β-d_4 and ether-d_{10} were not obtained, owing to faulty analysis. The total methane yield varies much less with deuterium substitution than does the hydrogen yield. Ratios of various isotopic methanes produced during radiolysis are shown in Table VI.

The G values of ethane and ethylene could not be determined because the various deuterated standards were not available. However, the relative concen-

Table IV. Hydrogen Yields from the Radiolysis of Deuterated Ethers

Ethyl ether	Phase	$\epsilon_p{}^a$	$G(H_2)$	$G(HD)$	$G(D_2)$	G(total hydrogen)	% D
$(C_2H_5)_2O$	Liquid	0.00	3.42	0.00	0.00	3.42	0
$(C_2H_5)_2O$	Liquid	0.17	0.92	0.00	0.00	0.92	0
$(CD_3CH_2)_2O$	Liquid	0.00	2.27	0.69	0.08	3.04	19
$(CD_3CH_2)_2O$	Liquid	0.17	0.57	0.21	0.04	0.82	20
$(CH_3CD_2)_2O$	Liquid	0.00	0.55	1.07	0.52	2.14	66
$(CH_3CD_2)_2O$	Liquid	0.17	0.27	0.29	0.11	0.68	48
$(C_2D_5)_2O$	Liquid	0.00	0.03	0.09	1.58	1.70	98
$(C_2D_5)_2O$	Liquid	0.17	0.07	0.15	0.29	0.51	84
$(C_2H_5)_2O$	Gas	0.00	6.44	0.00	0.00	6.44	0
$(C_2H_5)_2O$	Gas	0.17	1.64	0.00	0.00	1.64	0
$(CD_3CH_2)_2O$	Gas	0.00	4.40	1.47	0.14	6.01	17
$(CD_3CH_2)_2O$	Gas	0.17	1.00	0.32	0.08	1.40	19
$(CH_3CD_2)_2O$	Gas	0.00	1.18	1.90	0.72	3.80	58
$(CH_3CD_2)_2O$	Gas	0.17	0.49	0.44	0.12	1.05	41
$(C_2D_5)_2O$	Gas	0.00	0.10	0.08	3.07	3.25	97
$(C_2D_5)_2O$	Gas	0.17	0.18	0.26	0.29	0.73	70

^{a} ϵ_p = electron fraction of 1,3-pentadiene.

Table V. Methane Yields from the Radiolysis of Deuterated Ethers

Ether	Phase	$\epsilon_p{}^a$	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	Total methane
$(C_2H_5)_2O$	Liquid	0.00	0.42	0.00	0.00	0.00	0.00	0.42
$(C_2H_5)_2O$	Liquid	0.17	0.09	0.00	0.00	0.00	0.00	0.09
$(CD_3CH_2)_2O$	Liquid	0.00	0.068	0.039	0.033	0.237	0.018	0.40
$(CD_3CH_2)_2O$	Liquid	0.17	0.009	0.007	0.006	0.036	0.005	0.06
$(CH_3CD_2)_2O$	Liquid	0.00	0.189	0.175	0.011	0.000	0.000	0.38
$(CH_3CD_2)_2O$	Liquid	0.17	0.034	0.030	0.003	0.000	0.000	0.07
$(C_2D_5)_2O$	Liquid	0.00	0.017	0.019	0.000	0.054	0.41	0.50
$(C_2D_5)_2O$	Liquid	0.17	0.009	0.000	0.000	0.022	0.038	0.07
$(C_2H_5)_2O$	Gas	0.00	1.25	0.00	0.00	0.00	0.00	1.25
$(C_2H_5)_2O$	Gas	0.17	0.25	0.00	0.00	0.00	0.00	0.25
$(CD_3CH_2)_2O$	Gas	0.00	0.16	0.12	0.10	0.75	0.05	1.19
$(CD_3CH_2)_2O$	Gas	0.17	0.038	0.019	0.018	0.111	0.009	0.20

^{a} ϵ_p = electron fraction of 1,3-pentadiene.

Table VI. Ratios of Various Methanes Produced from the Ethers

Ether	Phase	$\epsilon_p{}^a$	CH_3D/CH_4	CHD_3/CD_4
$(CD_3CH_2)_2O$	Liquid	0.00	0.57	13.
	Liquid	0.17	0.8	7.
	Gas	0.00	0.75	15.
	Gas	0.17	0.50	12.
$(CH_3CD_2)_2O$	Liquid	0.00	0.92	...
	Liquid	0.17	0.88	...
$(C_2D_5)_2O$	Liquid	0.00	1.1	0.13
	Liquid	0.17	0.0	0.58

^{a} ϵ_p = electron fraction of 1,3-pentadiene.

Table VII. Per Cent Isotopic Composition of Product Ethylene

Ether	Phase	$\epsilon_p{}^a$	C_2H_4	C_2-H_3D	C_2-H_2D_2	C_2-HD_3
$(CD_3CH_2)_2O$	Liquid	0.00	7	14	52	27
	Liquid	0.17	9	13	47	31
	Gas	0.00	7	12	57	24
	Gas	0.17	12	11	54	23
$(CH_3CD_2)_2O$	Liquid	0.00	0	28	72	0
	Liquid	0.17	0	27	73	0
	Gas	0.00	5	15	75	5
	Gas	0.17	6	22	70	2

^{a} ϵ_p = electron fraction of 1,3-pentadiene.

trations of the isotopic ethylenes from ether-α-d_4 and -β-d_6 were measured from mass spectra obtained at a low bombarding energy (10.5 e.v.). Only the parent peaks of ethylene were obtained under these conditions, and it was assumed that the sensitivities of the various ethylenes were the same. The results are presented in Table VII.

Discussion

Gas Phase "Light" Ether. A mass balance of the products at 3.5×10^{20} e.v./g. was calculated. The products add up to an empirical formula of $C_{4.00}$-$H_{10.3}O_{1.00}$ and $G(-\text{ether}) = 11.2$. Thus, the products contain an excess of hydrogen which corresponds to $G(\text{excess } H_2) = 1.7$. It is unlikely that this is a result

of experimental error because a much higher degree of imbalance was found in the vapor phase radiolysis of cyclohexane,[6,7] and no imbalance was found in the vapor phase radiolysis of ethanol.[8] In the α-radiolysis of cyclohexane vapor at $108°$ $G(\text{excess } H_2) = 7.6^6$ and in the γ-radiolysis at $125°$ $G(\text{excess } H_2) = 7.0.^7$ In the α-radiolysis of ethanol vapor at $108°$ $G(\text{excess } H_2) = 0.0.^8$ The ether value falls between those of cyclohexane and ethanol, which is reasonable. The poor mass balances can be attributed to polymer formation

(6) J. M. Ramaradhya and G. R. Freeman, *J. Chem. Phys.*, 34, 1726 (1961).

(7) Calculated from results of J. Blachford and P. J. Dyne, *Can. J. Chem.*, 42, 1165 (1964).

(8) J. M. Ramaradhya and G. R. Freeman, *ibid.*, 39, 1836 (1961).

since the analytical systems could only measure compounds containing up to two monomer (ether or alkane) units. Polymer was observed on the reaction vessel walls after cyclohexane radiolysis.[9] In the ether system, the decrease in the yields of acetaldehyde and ethyl vinyl ether with increasing dose might be the result of polymerization reactions.

Ether vapor decomposes with a G value which is nearly the same as that in the liquid phase. ($G = 11.2$ and 11.3, respectively, based on the amount of C in the measured products. However, since G(excess H_2) = 1.7 in the vapor and 0.5 in the liquid radiolysis, the actual yield of ether decomposition is a few per cent larger in the vapor than in the liquid phase.) On the average, the ether molecules break into smaller fragments in the gas than in the liquid phase. The product distributions shown in Table II indicate that the following reactions are important in the gas phase.

$$C_2H_5O^* \longrightarrow CH_3CHO + H \tag{1}$$
$$\longrightarrow CH_3 + CH_2O \tag{2}$$
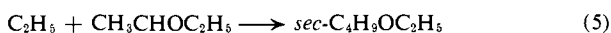$$C_2H_5^* \longrightarrow C_2H_4 + H \tag{3}$$
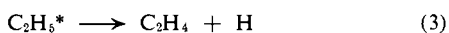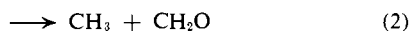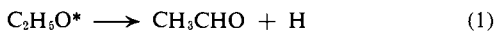
Reactions 1–3 would cause the ethanol and ethane yields to decrease, and the acetaldehyde, formaldehyde, hydrogen, methane, and ethyl isopropyl ether yields to increase on going from the liquid to the gas phase radiolysis.

Reactions 1–3 would occur to a smaller extent in the liquid phase because the excited radicals would be deactivated by collisions with the medium.

One reason for the smaller yield of methyl radicals in the liquid phase is probably the "cage" recombination reaction

$$CH_3 + CH_2OC_2H_5 \longrightarrow CH_3CH_2OC_2H_5 \tag{4}$$
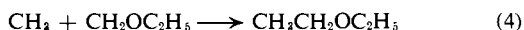
The yield of ethyl sec-butyl ether remained nearly unchanged whereas the ethane yield decreased threefold on going from the liquid to the gas phase radiolysis.

$$C_2H_5 + CH_3CHOC_2H_5 \longrightarrow sec\text{-}C_4H_9OC_2H_5 \tag{5}$$
$$\longrightarrow C_2H_6 + CH_2=CHOC_2H_5 \tag{6}$$
$$C_2H_5 + (C_2H_5)_2O \longrightarrow C_2H_6 + CH_3CHOC_2H_5 \tag{7}$$

The values of the ratio $G(C_2H_6)/G(sec\text{-}C_4H_9OC_2H_5)$ are 1.7 in the liquid and 0.53 in the gas phase, while those of $G(CH_4)/G(i\text{-}C_3H_7OC_2H_5)$ are 5.9 and 1.3, respectively. Both ratios are smaller in the gas phase. Assuming that values of $(k_{disproportionation}/k_{combination})$ are not smaller in the gas than in the liquid, the ratios indicate that the relative importance of radical–radical reactions is greater and that of radical abstraction (reaction 8) is less in the gas than in the liquid phase.

$$R + (C_2H_5)_2O \longrightarrow RH + CH_3CHOC_2H_5 \tag{8}$$
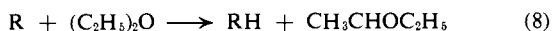
This can be explained as follows. The second-order rate constant of a bimolecular reaction that has a high collision efficiency will be diffusion controlled. Encounter frequencies of molecules such as diethyl ether in the liquid phase are an order of magnitude smaller, expressed as rate constants, than they are in the vapor phase.[10] Thus, rate constants of radical combination reactions will be an order of magnitude smaller in the

liquid than in the vapor. However, reactions that have low collision efficiencies can have larger rate constants in the liquid than in the vapor because collision frequencies, expressed as rate constants, are an order of magnitude larger in the liquid than in the vapor (owing to the "free volume correction"). Radical abstraction reactions usually have low collision yields (10^{-9} for $CH_3 + (i\text{-}C_3H_7)_2O \rightarrow CH_4 + C_3H_7OC_3H_6$ at room temperature[11]). Thus, the ratio of rates of $(R + M \rightarrow RH + R')/(R + R \rightarrow R_2)$ would be expected to decrease on going from the liquid to the gas phase.

The occurrence of radical–radical reactions in spurs in the liquid phase and the absence of spurs in the gas phase would tend to make the above-mentioned ratio larger in the gas than in the liquid. Since the observed ratios for methyl and ethyl radicals are smaller in the gas than in the liquid, the "spur effect" is smaller than the "rate constant effect" in these cases.

Gas Phase Inhibition. It is suggested that products of reactions of the type $R + R \rightarrow P$ and $R + M \rightarrow P$ were scavengeable by 1,3-pentadiene, whereas products of reactions of the types $M^* \rightarrow P$ and $R^* \rightarrow P$ were less readily affected by pentadiene in the ethyl ether system (see Figure 1 and Table III).

The fact that the ethylene yield was much greater than the ethanol yield supports the suggestion that ethylene was formed mainly by reactions such as (3). However, some of the ethylene and ethanol may have been formed by

$$(C_2H_5)_2O^* \longrightarrow C_2H_5OH + C_2H_4 \tag{9}$$
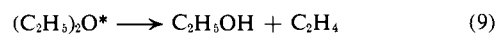
Deuterated Ethers. In contrast to the ethanol system,[12] substitution of D for H in the various groups in ether had the same effects in the liquid and gas phases. This is consistent with the suggestion that the differences observed between the phases in the ethanol system were due to the difference in the degree of hydrogen bonding in the two phases.[12] The discussion that follows refers to both phases in ether.

The value of G(total hydrogen) from ether-β-d_6 was only slightly smaller than that from light ether, whereas that from ether-α-d_4 was much smaller (Table IV). The effects of deuterium substitution in the two positions were roughly additive.

The percentage of D in the product hydrogen from ether-α-d_4 is much greater than that in the hydrogen from ether-β-d_6, in spite of the greater deuterium content of the latter molecule (Table IV).

These facts demonstrate that the α-C–H bond is the more reactive site in hydrogen formation. The same conclusion was reached in the ethanol system.[12]

The over-all isotope effect in hydrogen formation can be calculated from the ratio of the total hydrogen yields from ether and ether-d_{10}. The value is 2.0 in both the liquid and gas phases.

The percentage of D in the product hydrogen from ether-α-d_4 was significantly smaller in the inhibited than in the uninhibited systems, whereas that in the hydrogen from ether-β-d_6 was slightly larger in the inhibited systems (Table IV). Thus, the methyl group is relatively more important in the formation of unscavengeable hydrogen than it is in the formation of

(9) J. M. Ramaradhya, Ph.D. Thesis, University of Alberta, 1961.
(10) (a) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 271; (b) G. R. Freeman, *J. Chem. Phys.*, 33, 71 (1960), p. 78 and references therein.

(11) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1954, p. 622.
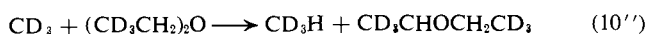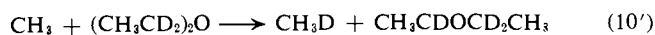(12) J. J. J. Myron and G. R. Freeman, *Can. J. Chem.*, in press.

scavengeable hydrogen. This is consistent with the idea that the unscavengeable hydrogen is formed from very reactive species that react with less selectivity than do those which form the scavengeable hydrogen.

A rate constant ratio and isotope effect involved in methane formation can be calculated using results from the liquid phase radiolysis of ether (Table VI). For simplicity it will be assumed that methane was formed only by the reactions

$$CH_3 + (C_2H_5)_2O \longrightarrow CH_4 + CH_3CHOC_2H_5 \qquad (10)$$

$$\longrightarrow CH_4 + CH_2CH_2OC_2H_5 \qquad (11)$$
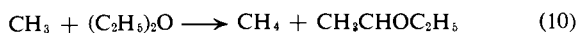
If methane were formed by other reactions, the rate constant ratio and isotope effect reported here could readily be transferred to those reactions. Approximate values of k_{10}/k_{11} and k_H/k_D can be calculated as follows.

$$CH_3 + (CH_3CD_2)_2O \longrightarrow CH_3D + CH_3CDOCD_2CH_3 \qquad (10')$$

$$\longrightarrow CH_4 + CH_2CD_2OCD_2CH_3 \qquad (11')$$

$$CD_3 + (CD_3CH_2)_2O \longrightarrow CD_3H + CD_3CHOCH_2CD_3 \qquad (10'')$$

$$\longrightarrow CD_4 + CD_2CH_2OCH_2CD_3 \qquad (11'')$$

From the data in Table VII, $k_{10}'/k_{11}' = 0.92$ and $k_{10}''/k_{11}'' = 13.0$ for the uninhibited reaction. If the crude assumption is made that the isotope effects in all of the reactions (10', 11', 10'', and 11'') are the same, then $k_{10}/k_{11} = (0.92 \times 13)^{1/2} = 3.5$ and $k_H/k_D = (13/0.92)^{1/2} = 3.8$. The inhibited methane yield is less than one-fifth of the uninhibited yield, so little error is introduced into the calculation of the kinetic parameters by using the total methane yields in calculating the values for the scavengeable reactions.

Similarly, $k_{10}/k_{11} = 2.5$ and $k_H/k_D = 2.9$ for the unscavengeable reactions. As expected, k_{10}/k_{11} and k_H/k_D are smaller for the unscavengeable than for the scavengeable methane-forming reactions because the more reactive species that form the unscavengeable methane react with less selectivity than do those which form the scavengeable methane. The above values of k_{10}/k_{11} and k_H/k_D are probably too small because of the considerable amount of isotopic scrambling in the ether-β-d_6 (see Table I).

In the radiolysis of liquid ether-α-d_4, 72% of the ethylene formed was $C_2H_2D_2$ (Table VII), which suggests that ethylene formation mostly involves β-C–H cleavage. The 28% of C_2H_3D indicates that α-C–H cleavage also contributes to ethylene formation.

The ethylenes from ether-β-d_6 confirm that both β- and α-C–H cleavage occur, with a preference for β-cleavage. The larger apparent amount of isotopic scrambling in the ethylene from ether-β-d_6 than in that from ether-α-d_4 is probably due to the larger amount of isotopic impurity in the ether-β-d_6.

It seems surprising that the ethylene compositions are so similar in the liquid and gas phase systems, in spite of the very different ethylene yields in the two phases.

The presence of 1,3-pentadiene had little effect on the isotopic distribution of the ethylenes.

Energy Transfer and Radical Scavenging in the Radiolysis of Solutions of p-Benzoquinone in Cyclohexane

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γ-Radiolysis of 40 mM benzoquinone in cyclohexane solutions gives the following products (the numbers are yields in molecules/100 e.v. absorbed in the whole solution): cyclohexene, 1.0; bicyclohexyl, 0.15; hydrogen, 3.1; monocyclohexylquinone, 4.4; hydroquinone (mostly as the quinhydrone), 3.1. Quinone is consumed with a G value of 10.8; quinone-containing products are formed with a G value of 10.6. Photolysis of saturated quinone solutions (40 mM) gives cyclohexylquinone and hydroquinone (as the quinhydrone); no cyclohexene or bicyclohexyl could be detected. The quinone recovered from a γ-irradiated solution of quinone in tritiated cyclohexane did not contain any radioactivity, indicating that quinone does not scavenge hydrogen atoms in this system under these conditions. These data are interpreted in terms of a set of processes which includes the scavenging of cyclohexyl radicals with a yield of 3.4 molecules/100 e.v. absorbed, deactivation of activated cyclohexane molecules by quinone with a yield of 2.3 (followed by reaction of about 50% of the activated quinone molecules with cyclohexane), and a "molecular" process for cyclohexene and hydrogen with a yield of 1.0.

Introduction

The presence of dissolved benzene, cyclohexene, or quinone in irradiated cyclohexane alters the yields of hydrogen, bicyclohexyl, and cyclohexene from the cyclohexane and results in the formation of new products. The nature of the interaction producing these changes depends upon the nature of the solute. In the case of benzene the interaction has been shown[1] to be partly one of radical scavenging and partly one of energy transfer; the interaction of cyclohexene during the radiolysis can be described almost entirely in terms of radical scavenging.[2] The purpose of this investiga-

(1) J. G. Burr, J. D. Strong, and F. C. Goodspeed, *J. Chem. Phys.*, **40**, 1433 (1964)
(2) M. Cher, C. Hollingsworth, and B. Browning, *ibid.*, **41**, 2270 (1964).